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(54) Recording medium for ink-jet printing

(57) A recording medium for ink-jet printing comprises a support material containing at least in the surface portion thereof a water-soluble salt of a metal having a valence of from 2 to 4, together with a cationic organic material.

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SPECIFICATION

Recording medium for ink-jet printing

The present invention relates to a recording medium for ink-jet printing, and more particularly to a recording medium for ink-jet printing capable of giving recorded images having high resistance to water.

Conventional inks for ink-jet printing contain, as colouring material, highly water-soluble colouring materials in order to achieve both stable ejection of the ink from the nozzles of the ink-jet printing apparatus, and high image density. Due to the use of highly water-soluble colouring materials, images recorded with conventional ink-jet printing inks readily spread and/or flow out in contact with water.

Various proposals have been made for overcoming the above disadvantage. For example, in Japanese Laid-Open Patent Application No. 55-150396, it is proposed to treat the surface of a recording medium by coating a solution of a water-resistant treatment agent thereon, after ink-jet printing in order to make the printed image resistant to water. However, then this proposal is adopted, the ink-jet printing apparatus tends to become over bulky and the application of the water-resistant treatment agent causes spreading of the printed images.

In accordance with another proposal disclosed in Japanese Laid-Open Patent Application No. 56-84992, the recording medium is treated with a polycationic electrolyte before it is used. This proposal, however, has the shortcoming that the printed images are so vulnerable to light that the recording medium is not suitable for practical use.

In a further proposal disclosed in Japanese Laid-Open Patent Application No. 56-86789, the surface of a recording medium is treated with a salt of multivalent metal so as to fortify the printed images. This method, however, has the shortcoming that the colour tone of the printed images is considerably changed by this treatment and it is not suitable for full-colour reproduction of images. Furthermore, this method has another shortcoming in that the applied metal salts come off the surface of the recording medium, in powder form, so that it is not suitable for practical use.

It is an object of the present invention to provide a recording medium for ink-jet printing which gives improved on resistance to both water and light of images recorded thereon.

The object of the present invention is attained by treating the surface of a recording medium for ink-jet printing with a water-soluble salt of a metal having a valence of from 2 to 4, together with a cationic organic material, the combined use of which in particular serve to improve the water-resistance of the printed images.

According to the invention, therefore, there is provided a recording medium for ink-jet printing comprising a support material containing at least in the surface portion thereof a water-soluble salt of a metal having a valency of from 2 to 4, together with a cationic organic material.

Examples of water-soluble metal salts for use in the present invention are salts of divalent calcium, divalent zinc, trivalent indium, trivalent aluminium cation, divalent magnesium and quadrivalent tin.

Specific examples of such salts include salts of divalent metals such as $MgCl_2$, $CaBr_2$, $Cacl_2$, $Ca(NO_3)_2$, CaI_2, $ZnCl_2$, $ZnBr_2$, ZnI_2, $Zn(ClO_3)_2$, $ZnSO_4$, $Zn(NO_3)_2$, SrI_2, $SrBr_2$, $SrCl_2$, $Sr(NO_3)_2$, $BaCl_2$, $Ba(NO_2)_2$, $Ba(OH)_2$, $Ba(OH)_2$, BaI_2, $BaBr_2$, $Fe(NO_3)_2$, $Ni(NO_3)_2$, $NiSO_4$, $NiCl_2$, $Cucl_2$ and $CuSO_4$; salts of trivalent metals such as $AlCl_3$, $Al_2(SO_4)_3$, $Al(NO_3)_3$, $ScCl_3$, $Sc(NO_3)_3$, $Sc_2(SO_4)_3$, $Ga(NO_3)_3$, $GaCl_3$, $Ga_2(SO_4)_3$, $InCl_3$, $Fe(NO_3)_3$ and alums; and salts of quadrivalent metals such as $TiCl_4$, $GeCl_4$, $Zr(SO_4)_2$, $SnCl_4$, $Sn(SO_4)_2$ and $Pb(CH_3COO)_4$.

Of the above water-soluble metal salts, $AlCl_3$, $Al_2(SO_4)_3$, $Al(NO_3)_2$, $ZnCl_2$, $ZnSO_4$, $SnCl_4$, $CaCl_2$, $MgCl_2$ and $InCl_3$ are particularly preferred.

The above water-soluble metal salts can be used alone or in combination and serve well to obtain whiteness, non-pollution, non-changing of the colour tone, high resistance to light (i.e., non-fading when exposed to light) and high resistance to water of the images recorded on the recording medium of the invention.

The amount of water-soluble metal salt in the recording medium is preferably from 0.1 to 10 g/m^2, more preferably from 0.4 to 3.0 g/m^2. If the water-soluble metal salt content is less than 0.1 g/m^2, the water-resistance and light-resistance of the printed images decrease, while if the metal salt content is more than 10 g/m^2, the water-soluble metal salts tend to come off the recording surface of the recording medium in powder form or the recording surface becomes sticky, so that when a pen using an aqueous ink is employed, the tip of the pen may be clogged with the metal salts and other materials in the recording surface.

As the cationic organic materials in the recording medium of the invention, there can be employed salts of alkylamines, quaternary ammonium salts, polyamines and basic latexes.

Specific examples of alkylamine salts are the acetates and chlorides of n-alkylamines containing from 10 to 20 carbon atoms.

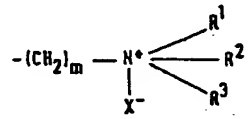
When such alkylamine salts are empl yed, the alkylamine salt content of the rec rding medium is preferably from 0.05 to 8 g/m^2, more preferably from 0.2 to 5 g/m^2. If the alkylamin salt content is less than 0.05 g/m^2, the water-resistance of the printed imagesis insufficient for practical use, while if it is more than 8 g/m^2, the light-resistance f the printed images decreases and the recording surface absorbs water and becomes sticky, so that when a pen using an aqueous ink is employed, the tip of the pen is easily clogged with the alkylamine salts and other materials in the recording surface.

Specific examples of suitable quaternary ammonium salts are lauryltrimethylammonium bromide, lauryltrimethylammonium chloride, cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, octalsoquinolinium bromide, octalsopquinolinium chloride, hexadecyltrimethylammonium bromide, and hexadecyltrimethylammonium chloride.

When such quaternary ammonium salts are employed, the quaternary ammonium salt content of the recording medium is preferably from 0.05 to 8 g/m^2, more preferably from 0.2 to 5 g/m^2. If the quaternary ammonium slt content is less than 0.05 g/m^2, the water-resistance of the printed images is insufficient for practical use, while if it is more than 8 g/m^2, the light-resistance of the printed images decreases and the recording surface absorbs water and becomes sticky, so that when a pen using an aqueous ink is employed, the tip of the pen is clogged with the quaternary ammonium salts and other materials in the recording surface.

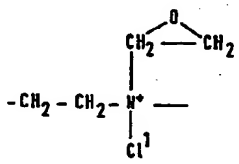
Specific examples of suitable polyamines are polyamide polyamines, polyoxyethylene alkylamines, polyethylamine epichlorohydrins, polydimethylaminoethyl methacrylates, and polyalkylammoniums.

Suitable polyethylene alkylamines are those having terminal groups of the formula



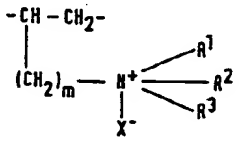
in which m is an integer of from 1 to 4, X^- represents Cl^-, OH^- or $RCOO^-$ and R^1, R^2 and R^3 are each hydrogen or a $C_1 - C_3$ alkyl group; the polymer having a molecular weight in the range of 1,000 – 100,000.

Suitable polyethylamine epichlorohydrins are those containing repeating units of the formula



the polymer having a molecular weight in the range of 1,000 to 100,000.

Suitable polyalkylammonium compounds are those containing repeating units of the formula



In which m, X^-, R^1, R^2 and R^3 have the meanings defined above. The polymers suitably have a molecular weight in the range 1,000 – 100,000.

Furthermore, basic latexes, such as polyamine latex and alkylammonium latex, can be employed. When these basic latexes are used, the latex content is preferably 0.2 to 25 g/m^2, more preferably 0.4 g/m^2 to 10 g/m^2. When latex content is less than 0.2 g/m^2, the water-resistance of the printed images is insufficient for practical use, while it is more than 25 g/m^2, the light-resistance of the printed images decreases and the recording surface absorbs water and becomes sticky, so that when a pen using an aqueous ink is employed, the tip of the pen is easily closed with the basic latex and other materials in the recording surface.

As commercially available cationic organic material, there may be mentioned San Fix 555 (Sanyo Chemical Industries, Ltd), polyamine cond nsates, Morin Fix 3p (made by Morimoto Chemicals Co. Ltd) and Fix FM (Made by Kuroda Kagaku Kogyo Co. Ltd), (the exact chemical compon nts and structures of these mat rials are n t known).

Recording media according to the invention may comprise a variety of types including single layer types (formed by immersing a suitable support in a solution or dispersion of the appropriate ingredients) or multi-layer types (formed by coating one or more layers containing one or more of the appropriate ingredients onto a suitable support).

Thus, a single layer recording medium can be prepared by immersing a support material, made of, for example, plain paper, non-sized paper or a plastic film capable of absorbing water, in a solution or dispersion of a mixture of one of the above water-soluble metal salts and one of the cationic organic materials, which mixture, as mentioned previously, serves to improve the resistance to water of the printed images and is hereinafter referred to as the water-resistance improving agent.

A multi-layered recording medium can be prepared by coating a surface layer onto a support material. The surface layer consists essentially of a binder, a pigment, the water-resistance improving agent and, possibly, small amounts of further additives. In the case of the multi-layered type recording medium, it is not always necessary that the support material is capable of absorbing water. It can be made of a non-water- absorbing material, such as paper consisting essentially of cellulose, synthetic paper, plastic film, glass, metal plate and metal foil.

Suitable binders for use in the surface layer, include resin-type binders and latex-type binders. Specific examples of resin-type binders include oxidized starches, etherified starches, esterified starches, dextrim, casin, gelatin, gum arabic, vegetable protein, cellulose, carboxymethylcellulose, hydroxyethylcellulose, cellulose derivatives, polyvinyl alcohol, polyvinylpyrrolidone, maleic anhydride resins, polyvinyl acetate, polyvinyl butyral, polyacrylamide, combinations of the above polymers, copolymers of the above polymers and modified polymers of the above polymers. Specific examples of latex-type binders include polyvinyl acetate latex, styrene-isoprene copolymer latex, styrene-butadiene copolymer latex, acrylic polymer latex, acrylic derivative – vinyl acetate copolymer latex, methyl methacrylate – butadiene copolymer latex, and combinatins and modifictions of the above latexes.

Specific examples of pigments for use in the surface layer include clay, talc, diatomaceous earth, calcium carbonate, calcium sulphate, magnesium carbonate, magnesium sulphate, barium sulphate, titanium oxide, zinc oxide, zinc sulphide, zinc carbonate, titanium white, aluminium silicate, silicon oxide, calcium silicate, aluminium oxide, aluminum hydroxide, and zeolite. Calcium carbonate, magnesium carbonate, barium sulphate and titanium white are most preferred.

Alternatively, a multi-layer recording medium can be prepared by coating on a support material a dispersion consisting essentially of a pigment and a binder (for example by blade coating, air-knife coating, bead coating, roll coating, wire bar coating, spray coating, gravure coating or reverse roller coating), and drying the coated dispersion by the application of hot air or heat thereto, with a coating deposition rate of from 0.1 to 60 g/m^2, more preferably from 3 g/m^2, to form a first layer on the support material. To the first layer, a liquid containing the water-resistance improving agent in an amount of from 0.1 wt. % to 30 wt. % is then applied and dried, to prepare recording medium.

The recording medium prepared as described above is by impregnating the support material with the water-resistance improving agentmay then be calendered at a temperature of from 50° to 200°C, more preferably from 60° to 120°C, under a pressure of from 10 to 150 kg/cm, more preferably from 50 to 80 kg/cm, whereby the recording performance of the recording medium can be improved.

In order that the invention may be well understood the following Examples are given by way of illustration only. In the Examples, all parts and percentages are by weight unless otherwise stated.

Example 1

A mixture of the following components was dispersed in a ball mill for 12 hours to prepare a dispersion.

	Parts
Calcium carbonate powder	45
Silica powder	25
Casein	3
Methylmethacrylate-butadiene copolymer latex (solid components)	25
Water	60
San Fix 555 (Sanyo Chemical Industries, Limited)	3

The thus prepared dispersion was applied to a sheet of high quality paper having a thickness of 95 μm by means of a doctor blade at a rate 15 g/m^2 (based on total solids), and was then dried at 120°C for 5 minutes. A 2% aqueous solution of aluminum chloride was applied by air-knife coating method onto the coated surface of the paper in a wet coating amount f 35 g/m^2, the applied solution was then dried at 110°C for 8 minutes, to give a recording medium. This recording medium was then calendered at 80°C under a pressure of 65 kg/cm, to provide an ink-jet recording medium according to the invention.

Ink-jet printing was then perf rmed on th thus prepared recording medium using a commercially available ink-jet printer (JP-4100 Printer made by Ricoh Company, Ltd), using an ink of the following formulation:

	Parts
C.I. Acid Red 92 (Daiwa Dyestuff Mfg. Co., Ltd.)	4
Diethylene Glycol	15
Glycerin	5
Deltop 33 (Takeda Chemical Industries Ltd.)	0.5
Water	75.5

The thus prepared recording medium and the images printed thereon were subjected to the following evaluation tests:

1. Surface Smoothness Test by Bekk Tester (Japanese Industrial Standards), by which the surface smoothness of the recording medium was measured.
2. Brightness Test by Hunter (Japanese Industrial Standards), by which the whiteness of the recording medium was measured.
3. GATF Color Evaluation Test with respect to Hue Error and Greyness, by which the hue error and the greyness of the printed images were evaluated.
4. Surface Hardness Test by Scratching of the Surface with Pencils (Japanese Industrial Standards), by which the strength of the recording surface layer of the recording medium was checked.
5. Printed Image Dryness Test

Ink-jet printing was carried out on the recording medium using the above-mentioned ink-jet printing apparatus. After printing, the recording medium was brought into pressure contact with a filter paper at intervals of 1 second, and the time at which no ink was transferred from the recording medium to the filter paper was checked, whereby the dryness of the printed images was evaluated.

6. Water Resistance Test of Printed Images

After printing on the recording medium, the recording medium was immersed in water at a temperature of 30°C for 1 minute. Thereafter, the change in image density was determined by comparing the image density before the immersion and the image density after the immersion. The change in image density was regarded as the image density fading ratio from which the water resistance of the printed images was assessed.

7. Light Resistance of Printed Images

The printed images were exposed to the light of a carbon arc lamp for 8 hours. The fading ratio of the reflected image density of the images was calculated in accordance with the following formula:

$$\frac{\text{Change in Image Density}}{\text{Initial Image Density}} \times 100$$

The results of the above tests are shown in Table 1.

Comparative Example 1

The procedure of Example 1 was repeated except that the step of coating with 2 v/v aqueous aluminium chloride solution was omitted. The thus prepared comparative recording medium was subjected to the same evaluation tests as in Example 1. The results are shown in Table 1.

Example 2

A mixture of the following components was dispersed in a homogenizer for 12 hours to form a dispersion.

	Parts
Silica powder	25
Calcium carbonate powder	45
Styrene-butadiene copolymer latex (solid components)	30
Polyvinyl alcohol (Kuraray 205)	5
Casein	3
Cetyltrimethylammonium chloride	1
Polyamine condensate (Morin Fix 3p made by Morimoto Chemicals, Inc.)	1
Water	70

The thus prepared dispersion was coated onto a sheet of medium quality paper having a thickness of 85 μm by a metal bar at a solids deposition rate of 10 g/m^2. The coating was then dried at 115°C for 12 minutes.

A 5% aqueous solution f aluminium nitrate has applied, by bead c ating, to the coat surface of the in a wet coating amount of 18 g/m^2. The applied solution was dried at 115°C under a pressure f 70 kg/cm, to prepare a recording medium according to the invention.

The thus prepared recording medium was subjected to the same evaluation tests as in Example 1. The results are shown in Table 1.

Comparative Example 2

The procedure of Example 2 was repeated except that the cetyltrimethylammonium chloride and the polyamine condensate were moitted from the formulation of the first layer formation liquid and the wet coating amount of the 5% aqueous aluminium nitrate solution was changed from 18 g/m^2 to 30 g/m^2.

The thus prepared comparative recording medium was subjected to the same evaluation tests as in Example 1. The results are shown in Table 1.

Example 3

A solution of the following components was prepared:

	Parts
Polyamine condensate (Flx FM made by Kuroda Kagaku Kogyo, Company, Ltd.)	5
Tin chloride	2
Water	93

The above solution was coated onto a commercially available recording paper for ink-jet printing (R-17 paper having a sizing degree of 3 sec) by air-knife coating at a wet coating rate of 25 g/m^2. The coated solution was then dried at 105°C for 12 minutes to give a recording medium was subjected to the same evaluation tests as in Example 1. The results are shown in Table 1.

Example 4

A mixture of a 5% solution of $AlCl_3$ and a 0.2 v/v solution of decylammonium acetate was coated onto a commercially available recording paper for ink-jet printing (M8 coated paper made by Mitsubishi Paper Mills, Ltd.) by bead coating at a wet coating rate of 40 g/m^2. The coated solution was then dried at 105°C for 10 minutes to give a recording medium according to the invention.

The thus prepared recording medium was subjected to the same evaluation tests as in Example 1. The results are shown in Table 1.

	Ex.1	C.Ex.1	Ex.2	C.Ex.2	Ex.3	Ex.4
Smoothness	220	210	640	610	80	190
Whiteness	82	82	84	84	81	82
Hue Error	40	39	42	45	48	42
Surface Hardness	H	H	HB	HB	—	H
Dryness (seconds)	1	1	1	1	1	2
Water-resistance	4%	6%	2%	15%	5%	2%
Light-resistance	7%	42%	6%	7%	9%	9%

As can be seen from the above results, the recording media according to the present invention have improved water-resistance and light resistance of the printed images without degrading the other properties as compared with the comparative recording media.

CLAIMS

1. A recording medium for ink-jet printing comprising a support material containing at least in the surface portion thereof a water-soluble salt of a metal having a valency of from 2 to 4, together with a cationic organic material.

2. A recording medium as claimed in Claim 1, in which the surface portion is a surface layer formed on the support material.

3. A recording medium as claim d in Claim 1 or Claim 2 in the water-soluble metal salt is a salt of divalent calcium, divalent zinc, trivalent indium, trivalent aluminium, divalent magnesium r quadrivalent tin.

4. A recording medium as claimed in any one of the preceding claims containing fr m 0.4 t 3.0 g/m^2 of the salt in the surface p rti n of the support material.

5. A recording medium as claimed in any one of the preceding claims in which the cationic rganic material is an alkylamine salt, a quaternay ammonium salt, a polyamine or a basic latex.

6. A recording medium as claimed in Claim 5, in which the cationic organic material is an alkylamine salt present in the surface portion f the support material in an amount of 0.2 t 5.0 g/m^2.

7. A recording medium as claimed in Claim 5 or Claim in which the alkylamine salt is an acetate or chloride of an *n*-alkylamine containing from 10 to 20 carbon atoms.

8. A recording medium as claimed in Claim 5 in which the cationic organic metal is a quaternary ammonium salt present in the surface portion of the support material in an amount of from 0.2 to 5.0 g/m^2.

9. A recording medium as claimed in Claim 5 or Claim 8 in which the quaternary ammonium salt is lauryltrimethylammonium bromide, lauryltrimethylammonium chloride, cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, octaisoquinolinium bromide, octaisoquinolinium chloride, hexadecyltrimethylammonium bromide or hexadecyltrimethylammonium chloride.

10. A recording medium for ink-jet printing as claimed in Claim 5, in which the cationic organic metal is a polyamine present in the surface portion of the support material in an amount of from 0.2 to 5.0 g/m^2.

11. A recording medium as claimed in Claim 5 or Claim 10 in which the polyamine is a polyamide polyamine, polyoxyethylene alkylamine, polyethylamine epichlorohydrin, polydimethylaminoethylmethacrylate or polyalkylammonium.

12. A recording medium as claimed in Claim 5 in which the cationic organic metal is a basic latex present in the surface portion of the support material in an amount of from 0.4 to 10 g/m^2.

13. A recording medium for ink-jet printing as claimed in Claim 5 or Claim 12 in which the basic latex is a polyamine latex or an alkylammonium latex.

14. A recording medium as claimed in any one of the preceding claim in which the surface portion further comprises a binder and a pigment.

15. A recording medium as claimed in Claim 1 substantially as hereinafter described with reference to the examples.

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